Optical Properties of ZnO Deposited by Atomic Layer Deposition on Sapphire: A Comparison of Thin and Thick Films

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Introduction

Zinc oxide (ZnO) is a wide direct bandgap (3.37eV) semiconductor that has versatile applications in photodetectors, bio-sensors etc. Large exciton binding energy of 60 meV at room temperature, bandgap tunability, high transparency, and high thermal and chemical stability, make it a promising candidate for optoelectronic devices. ZnO thin films can be deposited by atomic layer deposition (ALD) at growth temperature of 200ºC and below, which is essential for such applications as hybrid organic/inorganic junctions. Previously Guziewicz et al. found that with increasing the growth temperature from 100ºC to 300ºC, while keeping all the growth parameters constant, the stoichiometry of film changes. At growth temperature 100ºC films are O_2 rich and at T_g=300ºC they are Zn-rich conditions. Therefore growth temperature influences the type of defects created in the material. In the present study we have analysed thin layers of ZnO grown on a-plane sapphire substrate at different O_2 rich to Zn rich growth conditions and the results are compared with these obtained for thick ZnO films.

Experimental Method

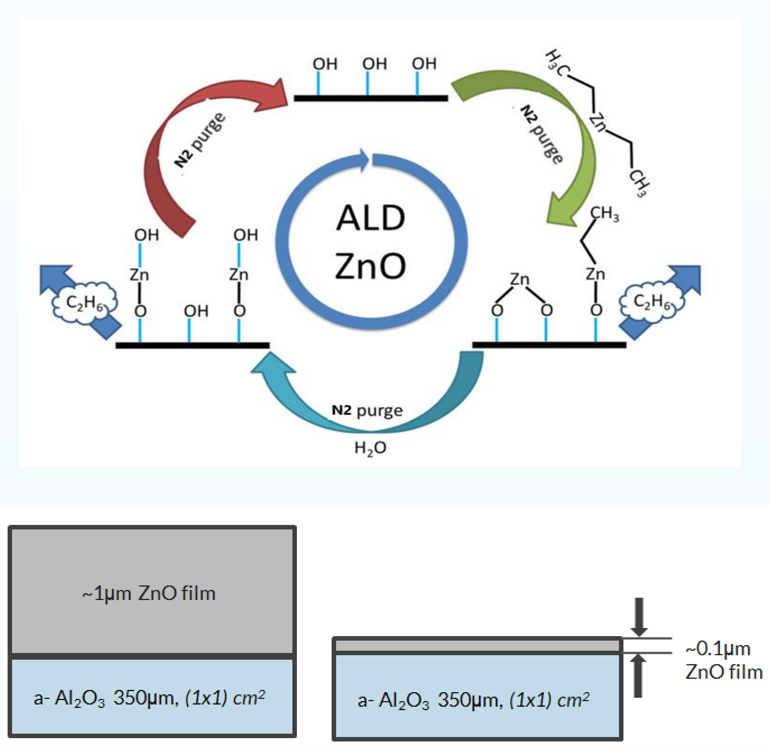
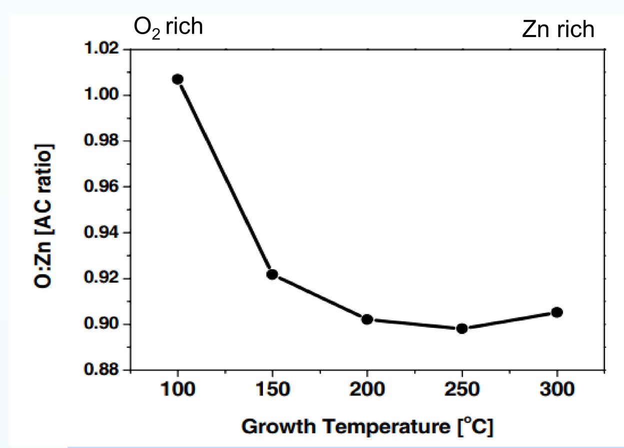


Fig.1. Schematic diagram of ALD process and ZnO/Al_2O_3 thick and thin film



Source: Guziewicz et al. Semicond. Sci. Technol. 27 (2012) 074011

As grown → RTP Annealed 800ºC, O_2 atm → **Optical analysis**
- UV-Vis spectroscopy
- Low temperature PL

Results and Discussion

1. UV- Vis Spectroscopy

Optical bandgap
- Optical bandgap calculated using Tauc relation

$$\alpha h\nu = A\,(h\nu - E_{g,o})^{1/2}$$

- $E_{g,o}$ of thin sample is higher than thick sample
- **RTA** causes widening of bandgap

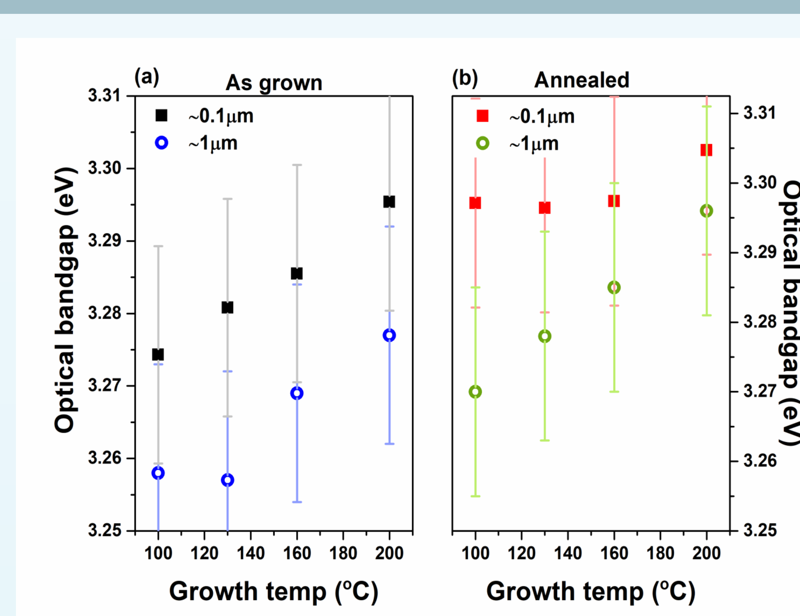


Fig.2.Optical bandgap for a) as-grown and b) annealed ZnO/Al_2O_3 samples grown at different temperatures.

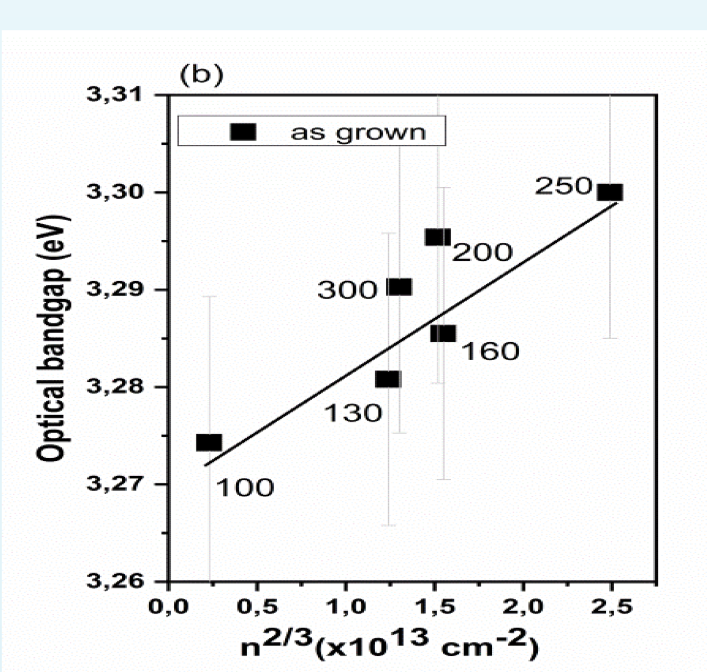


Fig.3. $E_{g,o}$ versus $n^{2/3}$ according to B–M effect for as-grown ZnO/Al_2O_3 thin films.

Burstein- Moss Effect
- Observed in degenerated or heavily doped semiconductor
- BM Energy can be calculated using relation

$$\Delta E_{BM} = \frac{\hbar^2 (3\pi^2 n)^{2/3}}{2m^*}$$

- Linear dependence of $E_{g,o}$ with $n^{2/3}$ in case of as grown sample attributed to BM effect

Intrinsic Bandgap
- Difference between $E_{g,o}$ and ΔE_{BM} is called **corrected** or **intrinsic bandgap**
- Both as grown and annealed samples follow a similar trend
- Intrinsic energy gap of annealed samples is higher than this of as grown one and does not change much with growth temperature

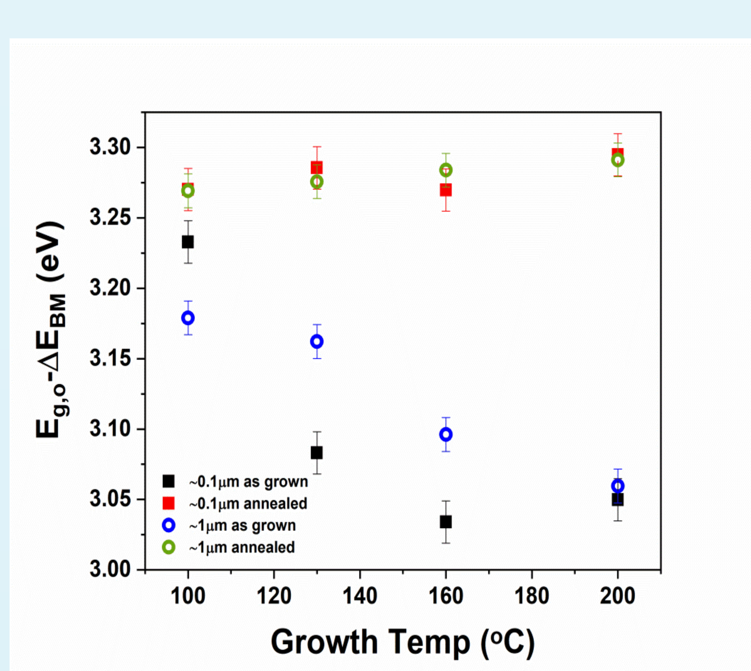


Fig.4. The corrected bandgap($E_{g,o}$-ΔE_{BM}) versus growth temperature for thick and thin ZnO/Al_2O_3 samples.

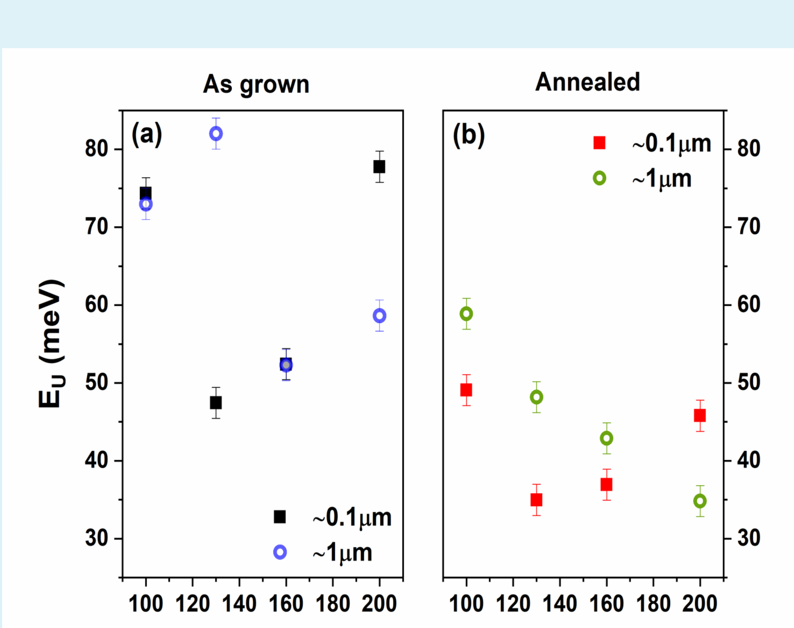


Fig.5. Urbach Energy for a) as-grown and b) annealed ZnO/Al_2O_3 samples grown at different temperatures.

Urbach Energy
- Related to **defects** or **disorder** in semiconductor
- α varies exponentially below the absorption edge
- $\alpha = \alpha_o\ exp[(h\nu)/E_U]$
- E_U is **higher** for **as grown samples**
- For $T_g \leq 160$ºC, disorder in thin sample is lower than in thick ones

2. Low temperature Photoluminescence

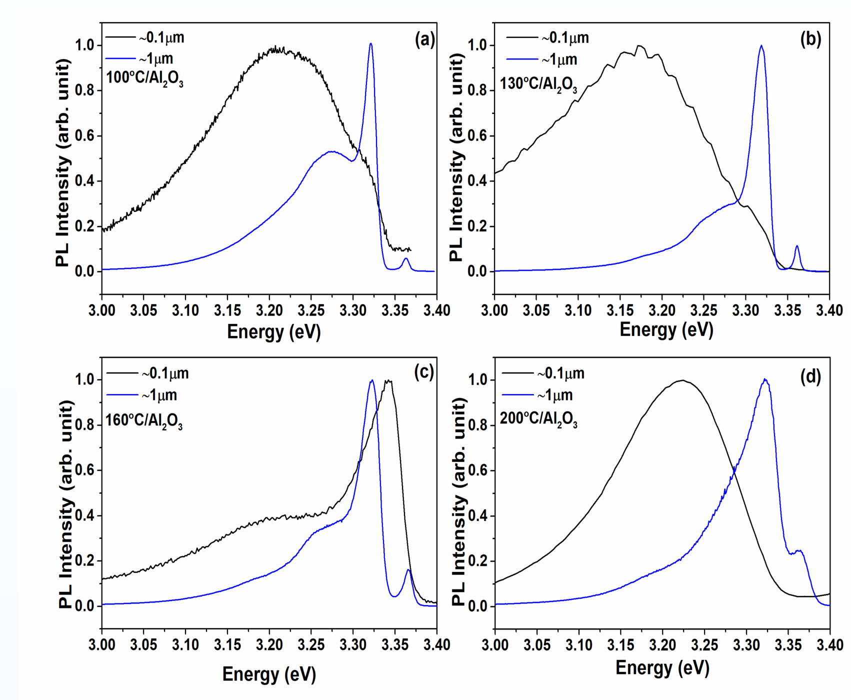


Fig.6. LT PL comparison of as-grown thin and thick ZnO/Al_2O_3 film at growth temperatures a) 100ºC, b) 130ºC, c) 160ºC, and d) 200ºC

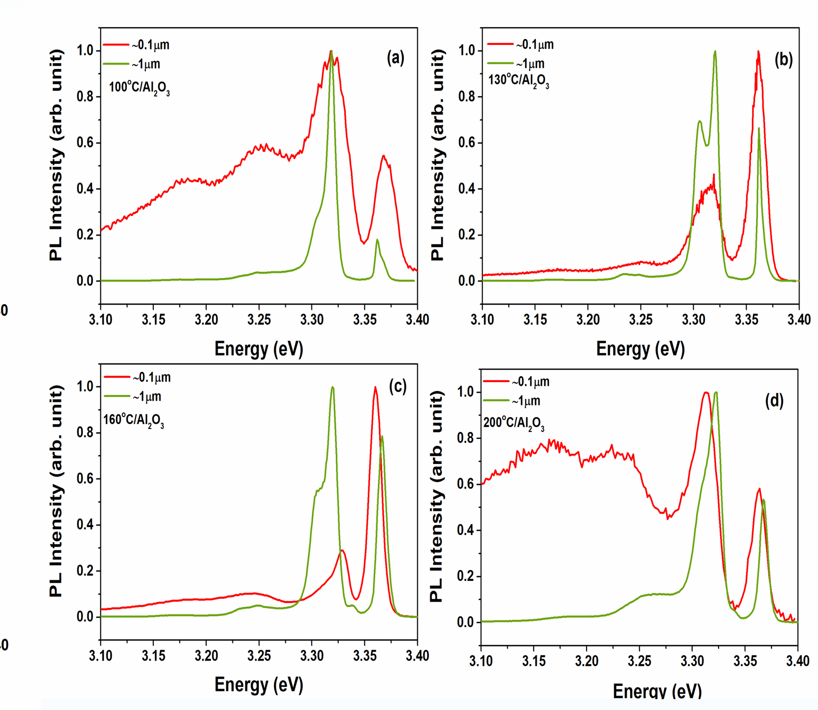


Fig.7. LT PL comparison of annealed thin and thick ZnO/Al_2O_3 film at growth temperatures a) 100ºC, b) 130ºC, c) 160ºC, and d) 200ºC

- Relative intensity of PL peaks at different growth temperature
- Peaks at 3.35-3.36 eV - **D^0X transition** and Peaks at 3.32 eV **- FA transition**
- Higher concentration of donor bound exciton states at growth temperature~160ºC
- **Narrower** PL peak for thick sample : better electronic property
- **FWHM decreases** after annealing

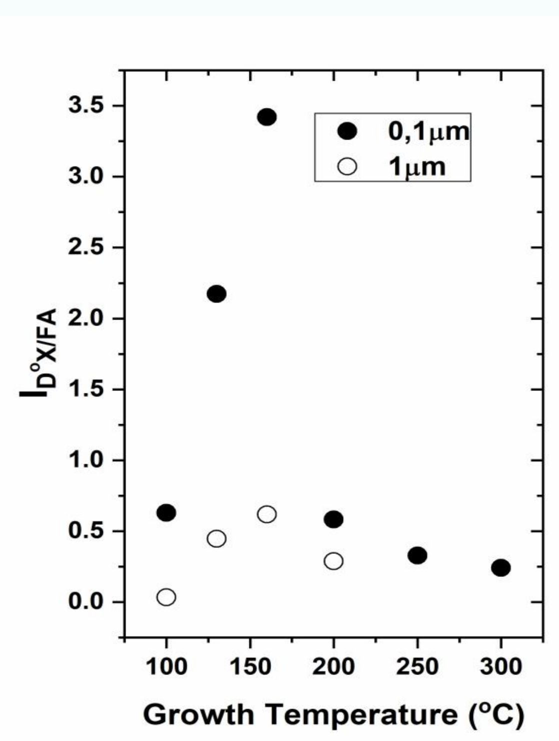


Fig.8. The relative intensity ratio of FA/D^0X peaks versus growth temperature for annealed ZnO/Al_2O_3 layers.

Conclusions

- Thin ZnO layers (thickness about 100nm) were grown on sapphire substrate at growth temperature 100ºC, 130ºC, 160ºC, 200ºC, 250ºC, and 300ºC
- Optical bandgap is higher for thin ZnO films as compared to thick ones. Annealing causes widening of bandgap
- For as grown samples, the intrinsic direct gap decreases with increase in applied growth temperature
- Intrinsic direct gap depends upon applied growth temperature rather than the thickness of samples. The behavior of the corrected energy gap can be associated with oxygen vacancy which occurs in different concentrations in layers grown under oxygen- or zinc-rich conditions and might be involved in the Zn_i–V_O or Zn_i–V_O–H complexes providing shallow donor states.
- High amount of defects and disorder we can expect in as grown samples
- Higher concentration of donor bound exciton states at growth temperature of~160ºC
- From LT PL study, significant narrowing of luminescence line is observed after annealing

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